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Technical

## Introduction

Tin is a metallic element belonging to group 14 of the periodic table, along with C, Si, Ge and Pb. The element has an atomic number of 50, an atomic mass of 119, three main oxidation states (-2, +2 and +4), of which the +4 state is by far the most common in nature, and ten naturally occurring isotopes, the largest number of all elements ( $^{112}\text{Sn}$ ,  $^{114}\text{Sn}$  to  $^{120}\text{Sn}$ ,  $^{122}\text{Sn}$  and  $^{124}\text{Sn}$ ), of which  $^{120}\text{Sn}$ ,  $^{118}\text{Sn}$  and  $^{116}\text{Sn}$  are the most abundant at 32.97%, 24.01% and 14.24% respectively of its mass. Tin shows intermediate characteristics in its chemistry between that of Ge and Pb.

Like Pb, Sn is a relatively rare metal, with an average crustal abundance of  $2.1 \text{ mg kg}^{-1}$ , but it is well known as a metallic element, because of its use in household products and the relative ease of its extraction from natural sources. It is one of the seven metals known in antiquity. Tin is a siderophile metallic element forming several minerals, including cassiterite  $\text{SnO}_2$  and the rarer stannite  $\text{Cu}_2\text{FeSnS}_4$ , but can also be present as an accessory element in biotite, muscovite, amphibole, sphene and rutile.

During magmatic processes,  $\text{Sn}^{4+}$  may replace  $\text{Ti}^{4+}$  and  $\text{Fe}^{3+}$  in accessory minerals such as sphene, ilmenite, rutile and magnetite. The small, highly charged  $\text{Sn}^{4+}$  ion is strongly concentrated as  $(\text{SnO}_4)^{4-}$  complexes in residual melts, and thus becomes enriched in felsic relative to mafic igneous rocks. Mielke (1979) cites values for the Sn content of igneous rocks as: ultramafic  $0.5 \text{ mg kg}^{-1}$ ; basalt  $1.5 \text{ mg kg}^{-1}$ , and granite  $1.5\text{--}3 \text{ mg kg}^{-1}$ . Tin is generally associated with oxygen in high-temperature minerals and sulphur at lower temperatures (Mielke 1979). In later stages of magmatic differentiation, Sn will become concentrated in the remaining melt until cassiterite  $\text{SnO}_2$  is formed, and Sn may also substitute for Cb, Ta and W. Cassiterite is often present as a disseminated accessory phase in evolved granite, and accumulates to economic levels in discrete hydrothermal veins and metasomatic deposits closely associated with highly siliceous lithologies (Ganeev *et al.* 1961, Ure and Berrow 1982). The main Sn carriers in granitic rocks are hornblende, biotite, muscovite, titanite, garnet, ilmenite and magnetite.

In sedimentary rocks, the concentration of Sn is primarily determined by the abundance of

resistate minerals such as cassiterite, sphene and magnetite. Small amounts of Sn dissolved during the weathering of mica may precipitate with Al-rich hydrolysates, thus accounting for the widespread accumulation of the metal in bauxite (Wedepohl 1978). Argillaceous and calcareous sediments typically contain Sn at levels in excess of the crustal average ( $4\text{--}6 \text{ mg kg}^{-1}$ ), while sandstone (*ca.*  $1 \text{ mg kg}^{-1}$ ) are generally depleted. In tropical soil, values of up to  $60 \text{ mg kg}^{-1}$  Sn have been recorded, with a large proportion held in clay and organic matter (Aubert and Pinta 1977). Mielke (1979) reports Sn levels of  $6 \text{ mg kg}^{-1}$  in shale, and  $<1 \text{ mg kg}^{-1}$  in sandstone and carbonate rocks. The average content of Sn in loess is given as  $5 \text{ mg kg}^{-1}$  (McLennan and Murray 1999).

The mobility of Sn during weathering is highly pH dependent and,  $\text{Sn}^{2+}$ , which is a strong reducing agent, is only present in acid and reducing environments (Kabata-Pendias 2001). Soluble Sn follows the behaviour of Fe and Al and remains in the weathered residue along with hydroxides of these metals. Tin forms soluble and insoluble complexes with organic substances. The occurrence of Sn in soil has not received much study. From the available data, Kabata-Pendias (2001) report a range of values varying from  $1$  to  $11 \text{ mg kg}^{-1}$  Sn with an average of  $1.1 \text{ mg kg}^{-1}$ .

In stream sediment, most detrital Sn is held in resistant oxide phases, such as cassiterite, which release Sn very slowly during weathering. Weathering of most natural and anthropogenic Sn carriers is intensified under acid, reducing conditions, although  $\text{SnS}_2$  is insoluble under reducing conditions (Brookins 1988). Any  $\text{Sn}^{2+}$  released oxidises rapidly and is subsequently bound to secondary oxides of Fe or Al as  $\text{Sn}(\text{OH})_4$  or  $\text{Sn}(\text{OH})_3\text{O}^-$ . The human-made organo-tin pesticide tributyltin readily adsorbs onto suspended particulate material (De Mora and Phillips 1997). In areas where Sn mineralisation is absent, Sn is an excellent indicator of contamination. Contaminated samples are often indicated by the presence of high levels of other metals such as Pb, Zn and As, which are not associated with Sn mineralisation. Concentrations of Sn in United Kingdom river water are typically

less than  $0.5 \text{ pg l}^{-1}$  (Neal and Robson 2000). Reimann and de Caritat (1998) claim average concentrations in stream water to be less than  $0.01 \text{ } \mu\text{g l}^{-1}$ .

Anthropogenic sources of tin include coal and wood combustion, waste incineration and sewage sludge (Reimann and de Caritat 1998). Other anthropogenic Sn sources include alloys such as solder (Sn-Pb), agricultural pesticides and wood preservatives in which organo-Sn compounds have been used.

Tin is believed to be an essential trace element in some organisms, potentially including humans, although its function has not been determined. Many Sn compounds are toxic to lower

organisms. Organo-tin compounds, which are persistent and not easily biodegradable, are of particular concern, for example in the well documented cases of shell abnormalities in shellfish and imposed in gastropods caused by tributyltin in anti-fouling paints for ships (De Mora and Phillips 1997). Toxic levels of inorganic Sn can cause growth depression and anaemia in humans, and also interferes with the metabolism of Zn, Cu and Ca (WHO 1996). Fortunately, Sn is poorly absorbed by the human body.

Table 62 compares the median concentrations of Sn in the FOREGS samples and in some reference datasets.

Table 62. Median concentrations of Sn in the FOREGS samples and in some reference data sets.

Tin (Sn)	Origin - Source	Number of samples	Size fraction $\mu\text{m}$	Extraction	Median $\text{mg kg}^{-1}$
Crust <sup>1)</sup>	Upper continental	n.a.	n.a.	Total	2.1
Subsoil	FOREGS	788	<2.0	Total (ICP-MS)	3.00
Topsoil	FOREGS	845	<2.0	Total (ICP-MS)	3.00
Soil <sup>2)</sup>	World	n.a.	n.a.	Total	4
Stream sediment	FOREGS	852	<0.15	Total (XRF)	2.25
Floodplain sediment	FOREGS	747	<2.0	Total (XRF)	2.00
Stream sediment <sup>3)</sup>	Canada	47 216	<0.18	Total (INAA)	1

<sup>1)</sup>Rudnick & Gao 2004, <sup>2)</sup>Koljonen 1992, <sup>3)</sup>Ganet 2006.

## Sn in soil

The median Sn content in both subsoil and topsoil is  $3 \text{ mg kg}^{-1}$ , and slightly less than half the values are below the detection limit of  $2 \text{ mg kg}^{-1}$ . The maximum value in both subsoil and topsoil is  $106 \text{ mg kg}^{-1}$  Sn. The average ratio topsoil/subsoil is 1.134.

Low Sn values in subsoil ( $<2 \text{ mg kg}^{-1}$ ) occur in Ireland, northern Britain, large parts of Fennoscandia, the Baltic states, Poland, northern Germany, part of northern France and adjacent Belgium, central Hungary, the Dalmatian coast of Croatia, Albania, northern and southern Greece, and south-east Spain.

In subsoil, Sn shows high values ( $>5 \text{ mg kg}^{-1}$ ) in south-west England, southern Brittany, the Massif Central, the Erzgebirge, the Black Forest, western Austria, the Central Iberian Zone of

northern Portugal and western Spain (granitic basement, and some W-Sn mineralisation), one point anomaly in north-east Greece (with the highest Sn value near to the Simvolos granite). In most cases enrichment can be traced back to known ore deposits or tin-bearing districts. The distribution map for W shows some resemblance, but on closer inspection the point anomalies of W seldom coincide with the highest Sn values.

There are some minor differences between the subsoil and topsoil Sn distribution maps. A slight enrichment occurs in topsoil, as indicated by the average ratio topsoil/subsoil of 1.134.

In subsoil, Sn shows a good correlation ( $>0.4$ ) with Ta, Be, Th, Cs, Bi, Tl, Rb and Y, and a weak correlation ( $>0.3$ ) with Ce, Nb, Ga, In, U, As and Zn. This pattern is very similar in topsoil. The

association with Be, Bi, As, Ta, Nb, Cs and Rb points to the leucogranitic/ greisen association,

typical for tin mineralisation.

#### Sn in stream sediment

The median Sn content in stream sediment is  $2.10 \text{ mg kg}^{-1}$ , with a range varying from  $<1$  to  $188 \text{ mg kg}^{-1}$ . About 22% of the values are below the detection limit.

The Sn stream sediment distribution map shows low areas ( $<1 \text{ mg kg}^{-1}$ ) throughout most of Finland, central and northern Norway, the Baltic states, the northern European lowlands in Poland, Denmark, Netherlands and north-western Germany, central Austria, eastern Hungary and parts of Greece.

High Sn values in stream sediment ( $>4.0 \text{ mg kg}^{-1}$ ) occur mainly in southern England (with anomalous values in Cornwall), a large area in France over the Massif Central and extending into Brittany, the Vosges Mountains, the northern Bohemian Massif, southern Norway, the Central Iberian Zone of northern Portugal (where W-Sn

mineralisations are known) and western Spain (granitic basement with mineralisation), Corsica and the alkaline magmatic province in Italy. In most cases, the high Sn values can be traced back to known ore deposits or tin-bearing districts. A point anomaly appears over the Moume granite in northern Ireland, and in Attica, Greece, where it may either indicate unknown mineralisation or contamination by industrial activities.

Tin in stream sediment has a good positive correlation ( $>0.4$ ) with Ta, W, Y, Rb, U and Th, and a weak correlation ( $>0.3$ ) with Cd, Tl, Cs and most REEs. This is caused by the leucogranitic/ greisen association characterising tin mineralisation or enrichment, possibly enhanced in stream sediments by the gravity concentration of heavy minerals such as cassiterite, tantalite, wolframite, xenotime and monazite.

#### Sn in floodplain sediment

Total Sn values in floodplain sediment vary from  $<1.0$  to  $649 \text{ mg kg}^{-1}$ , with a median of  $2.0 \text{ mg kg}^{-1}$ ; it is noted that about 25% of the XRF determinations are below the detection limit of  $1 \text{ mg kg}^{-1}$ . Therefore, the variation in the lower Sn values is constrained by the detection limit of the analytical method.

Low Sn values in floodplain sediment ( $<1.00 \text{ mg kg}^{-1}$ ) occur in the north of Europe over most of Finland and Sweden on the Precambrian crystalline rocks; parts of Norway, and north Scotland on predominantly Caledonide metamorphic rocks; most of Ireland on limestone, elastics and crystalline rocks; glacial drift covered north-west Germany, and over the glacial drift covered plain extending from Poland to the Baltic countries; in southern Europe, low Sn values are found in small areas in southern Spain on clastic and calcareous rocks, southern Italy with Tertiary sediments, and the calcareous Dalmatian coast of Croatia, and central Greece on clastic, carbonate and ophiolitic rocks.

High values Sn in floodplain sediment ( $>4.00 \text{ mg kg}^{-1}$ ) occur in the Variscan areas of south-west England (Camborne-Redruth Sn-W), northern

Portugal (can be associated to the drainage of the W-Sn Panasqueira mine), and adjacent part of Spain associated with the Extremadura and Pedroches granite batholiths; Galicia in north-west Spain (Santa Comba Sn-W, Fontao Sn-W-Mo, San Finx W-Sn-Mo) and adjacent areas of Zamora and Salamanca with Sn-W mineralisations; the Bilbao anomalous zone draining calcareous rocks and shale is ascribed to industrial contamination; in France along the Pyrenees, and over the Massif Central to Brittany, associated with granite and mineralisation (e.g., Abbaretz Sn, Echassieres Li-Sn-Be-Ta); near the German-Czech border (Altenberg Sn-Ag, Cinovec Sn-W deposits in the Erzgebirge); and northern Sardinia (granite).

The point Sn floodplain sediment anomaly in the Vesdre basin of Belgium is attributed to pollution by metallurgical activities. Further, large areas with high Sn values in France, central Britain and Germany, not associated with mineralisation, are suspected to be caused by agricultural pollution (possible use of organo-Sn pesticides, which should however be investigated). The high Sn value in floodplain

sediment near Glasgow in Scotland may be related to volcanic rocks of the Midland Valley, but is more likely to be of industrial origin.

Several outliers of Sn in floodplain sediment are present in two Variscan areas that were close together before the opening of the Bay of Biscay: south-west England with the Dartmoor granite ( $649 \text{ mg kg}^{-1}$ ) and Saint Austell granite ( $118 \text{ mg kg}^{-1}$ ), and northern Portugal with three highly anomalous points (260, 238 and  $181 \text{ mg kg}^{-1}$ ), all related to mineralisation.

Tin in floodplain sediment shows a good correlation with As, Ta, Rb and W, and a weak correlation with Be, Li, Tl, Nb, Cs, Th and U.

In conclusion, high Sn values in floodplain sediment are related to granite intrusives hosting mineralisation. However, there are high Sn values in France, central Britain and Germany, which are not directly associated with mineralised granite, and are suspected to be caused by agricultural pollution, and others by industrial processes (e.g., Bilbao in Spain and Vesdre basin in Belgium).

#### Sn comparison between sample media

Patterns in Sn distribution between all solid sample media are broadly similar, although there are some significant differences. Compared to soil, stream sediment is higher in Sn in southern Norway, Britain, central Italy, Corsica, Albania and in the border area between Poland and the Czech Republic. Floodplain sediment (and to a lesser extent stream sediment) is enhanced throughout France, and in a belt extending from central Germany to the Czech Republic influenced by the mineralisation and historical mining of the

Erzgebirge. There is a depletion in sediment Sn concentration in the coastal area of Croatia compared to soil concentrations. A boxplot comparing Sn variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 44.

Stream water data have been rejected on the grounds that a significant number of samples were contaminated during sampling and subsequent storage prior to analysis.

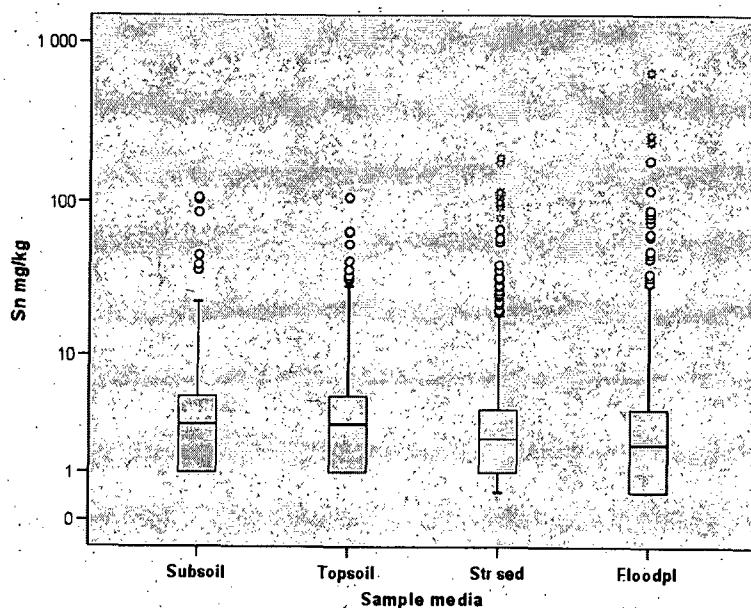


Figure 44. Boxplot comparison of Sn variation in subsoil, topsoil, stream sediment and floodplain sediment.



## Chemical Speciation of Lead Dust Associated with Primary Lead Smelting

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### Introduction

### Methods

### Results and Discussion

### Abstract

The research presented in this article assessed geochemical factors relating to dust produced during primary lead smelting. Bulk dust samples and size-selective airborne dust samples were collected from four areas of a primary lead smelter and analyzed by X-ray diffraction and sequential chemical extraction. X-ray diffraction showed that the smelter dusts were composed primarily of sulfides, oxides, sulfates, and silicates of metal ores, with galena being the primary dust component. Sequential extraction revealed the solubility of lead compounds at less than 7% in the exchangeable and mildly acidic steps for the bulk dusts collected from four smelter areas. The later steps of the extraction procedure were more effective in dissolving the lead compounds associated with the bulk dust samples, with 43%, 26%, and 8% of the total lead, in the ore storage, sinter, and blast/dross smelter areas, respectively, being extracted in the residual step. Sequential extraction of coarse airborne dust samples from the ore storage and sinter plant showed that 1.2% and 4.1% of the total lead, respectively, was exchangeable. The finer particle size fractions from these areas of the smelter showed higher percentages of exchangeable lead. Of the coarse airborne dust from the blast/dross furnace processes, 65% of the total lead was exchangeable. However, the largest percentage of lead from these areas was associated with the finer particle-size fractions. If lead bioavailability is related to its solubility as determined through sequential extraction, the health hazards associated with lead exposure may be appreciably enhanced in the blast and dross furnace processes. Key words: bioavailability, lead dust, lead speciation, sequential extraction. Environ Health Perspect 106:565-571 (1998). [Online 11 August 1998]

<http://ehpnet1.niehs.nih.gov/docs/1998/106p565-571spear/abstract.html>

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## Introduction

The research presented here was performed in a primary lead industry as part of a larger study designed to evaluate worker exposure to lead in terms of new health-related criteria. The aim of the overall study was to compare current worker exposure levels in terms of the relevant aerosol fractions of inhalable, thoracic, and respirable lead (1).

To completely assess the risk associated with lead aerosol exposure, the physical and chemical properties as well as the size distribution of the aerosol must be known. Absorption of lead from the respiratory and/or gastrointestinal tract is influenced by particle size, the pattern of regional particle deposition, and particle solubility. Particles larger than 3  $\mu$ m in diameter deposit primarily in the nasopharyngeal and tracheobronchial regions of the respiratory tract and can be transferred by mucociliary transport to the esophagus and swallowed (2). Particles smaller than 3  $\mu$ m have a greater probability of depositing in the alveolar regions of the respiratory tract. Bioavailability has been defined as the fraction of a compound in a matrix that is released from that matrix and absorbed into the body's blood plasma (3). An important parameter relating to bioavailability is solubility, which is related to the ability of a compound to reach that location in the body where it can exhibit its inherent toxicity. Many factors determine the degree to which lead, when inhaled or ingested, can become soluble and enter the bloodstream. These factors include the site of contact, pH of the body fluid contacted, residency time, nutritional status, and numerous geochemical factors.

The major geochemical factors controlling the availability of lead from dust and/or soils include the species of lead, the size of the lead-containing particles, and the matrix incorporating the lead species (4). All species of lead compounds deposited in the deep lung region (alveoli) are thought to be completely absorbed into the bloodstream (5-7). However, larger lead particles, which may have indefinite residency times in the upper regions of the respiratory tract or may be transferred from the respiratory tract to the stomach, will be absorbed at different rates based largely on speciation. Lead in the form of a sulfide is less bioavailable than lead carbonate or lead oxide (8).

The species of lead incorporated into soil vary depending on the source of lead. Soil mineralogy associated with lead smelter sites is complex, with lead existing as sulfides and multimetal oxides. Foster and Lott (9), in a study of lead speciation at a lead smelter, reported that galena was the major constituent of airborne lead particles from ore handling operations, and lead oxide species were the constituents of airborne particles associated with actual smelting operations such as the blast furnace and dross plant.

Chemical sequential extraction techniques have been developed to assess the solid-phase solubility or chemically extractable percentages of heavy metals occurring in contaminated soils, industrial and municipal sludges, and dusts. These techniques use chemical reagents of various strengths and pHs to leach metals from contaminated materials. The solutions are designed to interact with a solid contaminated material and liberate heavy metals on the basis of the solubility of the metal species within that solvent. Harrison et al. (10) suggested that mobility and bioavailability of metals decrease approximately in the order of the extraction sequence. Jenne and Luoma (11) showed that the bioavailability of heavy metals was inversely related to the strength of the metal-particulate binding in sediments. Other studies have demonstrated that compounds that are readily dissolved in weak acid are highly bioavailable (12,13).

The limitations of chemical sequential extraction techniques involve uncertainties as to the selectivity of the various extractants and readsorption of dissolved ions back onto the solid material. Chemical speciation and amount of material leached may result in a redistribution of metals within the leach fractions which is not representative of the sample. Despite these limitations, sequential extraction can provide qualitative information that may aid in the prediction of the bioavailability, mobilization, and transport of heavy metals (14). The research described in this paper was

designed to assess the geochemical factors relating to lead in a primary production industry through the use of the Tessier sequential extraction method (15) with modifications developed by Harrison et. al. (10).

## Methods

**The workplace studied.** The primary lead industry where this study was carried out processes concentrated lead, zinc, copper, and silver sulfide ores. Ores from mines around the world arrive at the smelter by truck or rail. Upon arrival, samples from each ore source are analyzed in the mill building to determine their elemental composition and moisture content. After sampling, ores are transported to a large ore storage building, where they are removed by overhead crane into either storage piles or large concrete feeder bins. Here materials are aggregated according to their chemical composition. These stored materials are subsequently routed by conveyor to the sinter plant where the ore is combined with fuel, ignited, and burned to produce fused "sinter" material (during which process the sulfur content is reduced). During sintering, the sulfides are oxidized to sulfates at approximately 700°C to produce a porous solid material composed primarily of bound lead oxides, lead sulfates, and lead silicate aggregates. The resultant sinter is then crushed and graded. The crushed sinter is mixed with coke and iron and transported to the top of the blast furnace into which oxygen-rich air is blown. In the blast furnace, the sinter is extensively reduced at 1,000-12,000°C to produce molten lead, tin-arsenic-silver sulfides (speiss), copper-iron sulfide (matte), and iron silicate (slag). The molten material descends to the bottom of the blast furnace and collects in a settling basin, where the molten lead-rich fraction settles to the bottom and the lighter "slag" comes to the surface. The slag contains the iron which has been added, as well as zinc and lime. The lead fraction and slag are separated by draining the molten material out of the basin by ports located at different heights on the basin. Before cooling, small railcars are used to transport the slag for disposal and the lead-rich fraction to the dressing plant. In the dressing plant, elemental lead is separated from impurities not eliminated in the blast furnace. The molten material from the blast furnace is poured into a large kettle, heated, and allowed to cool slowly. As the kettle cools, the impure "dross" fraction, rich in copper and arsenic, rises to the surface. This dross is skimmed off the top of the cooling kettle and transported to a large reverberatory furnace. The remaining pure lead is poured into molds and shipped to a refinery for further processing. The dross material in the reverberatory furnace is again heated and allowed to cool slowly. During cooling, three distinct layers are formed. The top "matte" layer is rich in iron and copper; the middle "speiss" layer is rich in arsenic. These two layers are tapped from the reverberatory furnace and shipped to a different smelter for copper extraction. The bottom layer contains pure lead and is returned to the dressing kettles for further extraction.

**Sampling technique and locations within the smelter.** Samples for lead speciation analysis were collected as both bulk dust and air samples. We collected bulk samples from four areas of the smelter: off-loading and ore storage, sinter plant, blast furnace, and dross furnace. The bulk dust samples were taken from dust-laden surfaces such as walkways or work surfaces using spatulas. The spatulas were cleaned using alcohol wipes after each collected sample to avoid cross-contamination. The collected material was placed in labeled petri dishes, sealed, and transported to the laboratory.

We collected air samples using a 28.3 l/min Andersen multistage cascade impactor placed in each of the four areas of the smelter described above. The Andersen was chosen for air sampling for two reasons: 1) large sample masses can be collected on the sampling stages because of the large sampler air volume rates, and relatively large sample masses are required for speciation analysis, and 2) a knowledge of the aerodynamic dimension of particles in the work environment is vital to understanding their potential health effects. The Andersen cascade impactor allows for the simultaneous determination of concentration and particle sizing information in one sample. The sampler is designed to reproduce to a reasonable degree the dust-collecting characteristics of the human respiratory system (16). The Andersen sampler is a static sampling instrument that consists of eight aluminum stages held together by three spring clamps and gasketed with O-ring seals. The eight stages of the impactor are preceded by a preseparator, designed to prevent particle bouncing and reentrainment errors, by limiting the access of larger particles to the sizing portion of the instrument. Cascade impactors operate on the principle of inertial impaction. A given stage consists of radial or circular slot openings and its accompanying impaction surface. The slot diameters become smaller at each successive stage proceeding through the impactor, resulting in successive increases in air velocity at each stage. Particle impaction is determined by its aerodynamic diameter ( $d_{ae}$ ), with particles of larger  $d_{ae}$  being impacted on the upper stages and particles of smaller  $d_{ae}$  being impacted on the lower stages. For the Andersen sampler operated at 28.3 l/min, particle fractionation ranges from 10.0 to 0.4  $\mu$ m. The particle size ranges for each stage of the Andersen sampler and their relationship to the human respiratory tract are shown in Table 1.

Andersen stage no.	Particle aerodynamic diameter ( $\mu$ m)	Respiratory tract region*
Preseparator	>10	Nasopharyngeal
Stage 0	8.0-10.0	Nasopharyngeal
Stage 1	5.0-8.0	Nasopharyngeal and tracheobronchial
Stage 2	4.7-5.6	Nasopharyngeal and tracheobronchial
Stage 3	3.3-4.7	Nasopharyngeal and tracheobronchial
Stage 4	2.1-3.3	Tracheobronchial and alveolar
Stage 5	1.1-2.1	Alveolar
Stage 6	0.80-1.1	Alveolar
Stage 7	0.43-0.85	Alveolar

\*Respiratory tract particle deposition has been estimated from mathematical models and human inhalation experiments. There is variability in particle deposition by particle size in the different regions of the respiratory tract. Deposition of submicron particles (<1  $\mu$ m) can occur in the sample stages from Stage 2.

In this research, cellulose acetate filters of 82-mm diameter were placed on inverted stainless-steel impaction plates located on each stage. We used cellulose acetate filters because of their low trace metal background levels. Particles that reach the internal stages were assumed to stay on the impaction surface or filter. Air was drawn through the impactor by a 12-V AC Andersen pump operated at a calibrated flow rate of 28.3 l/min.

Air samples from the Andersen were combined to ensure that enough sample was available for speciation analysis. The samples from stage 0 were combined with stage 1 samples; samples from stages 2, 3, and 4 were combined; and samples from stages 5, 6, and 7 were combined for each of the Andersen samples collected from the different smelter areas. Because of the small amount of material collected in the blast furnace area using the Andersen sampler, the blast and dross furnace air samples were combined into one sample group for analytical purposes. The bulk dust samples from these two areas were also combined into one sample group to maintain consistency with the air sample analysis.

**Sample analysis.** The bulk dust samples and the airborne dust collected on the first two stages of the Andersen sampler were analyzed by X-ray diffraction to determine the spectrum of metal compounds present in the dusts from the four smelter processes. Dust collected on the final six stages of the Andersen sampler was not analyzed by X-ray diffraction due to the small sample mass accumulated on these stages. Next, both the bulk dust samples and the airborne dust samples from all the stages of the Andersen samples were analyzed by a series of sequential chemical extractions. The sequential chemical extractions, as well as the X-ray diffraction analysis described above, were performed at the Montana Tech of The University of Montana physical chemistry laboratory. One of the most thoroughly researched extraction techniques for studying chemical associations of metals in soils is the method of Tessier et al. (15). This procedure identifies specific classifications of heavy

Classification	Form of association	Extraction technique
Social	Word co-occurrence, coreference	Heads-to-tails path with error rates
Exchangeable	Specificity identified, no exchangeable	Word co-occurrence with semantic context
Characteristics phase	Pre-association or co-association	Heads-to-tails mild select
For-then added phrase	Specificity identified, no co-association	Mild select
Organic phrase	Comp. linked, identified	Quads
Physical phrase	In mental form	Quads with strong select

Fraction	Procedure
Exchangeable	1.0M $\text{MgCl}_2$ , pH 7H 1 hr, 20°C, continuous agitation
Carbonate	1.0M $\text{NaOAc}$ , pH 5H 5 hr, 20°C, continuous agitation
F-soluble acids	0.2M $\text{HNO}_3$ in 85% methic acid, 6 hr, 95°C, occasional agitation
Organic	0.2M $\text{HNO}_3$ + 30% $\text{H}_2\text{O}$ , 6.5 hr, 95°C, occasional agitation Further 2.0M $\text{HNO}_3$ , pH 2.0 6 hr, 95°C, occasional agitation 0.2M $\text{HNO}_3$ (6.11 mixture), 6 hr, 95°C, continuous agitation
Residual	2 + 20% $\text{HNO}_3$ , 10 min to extract, 4M $\text{HNO}_3$ (residual extraction), 2 hr, 200 ml water new dryness, 1 ml conc nitric acid of a new origin to dryness, 6 hr, 100 ml water up to 5 ml concentrated $\text{HCl}$ and diluted to 50 ml or 250 ml with double deionized water

Mineral	Chemical formula	Constituent
<b>Dry storage area bulk dust sample</b>		
Silica, am	PS	Major1
Alumina, am	PS <sub>2</sub> O <sub>3</sub>	Minor2
Stibnite	Pb <sub>3</sub> Sb <sub>2</sub> S <sub>6</sub>	Minor2
Isodimorph titanium oxide	Pb <sub>2</sub> (TiO <sub>3</sub> ) <sub>2</sub>	Minor2
Isodimorph phosphite	Pb <sub>2</sub> (PO <sub>3</sub> ) <sub>2</sub>	Minor2
Isodimorphite	Pb <sub>2</sub> As <sub>2</sub> S <sub>6</sub>	Minor2
Lead oxide	Pb <sub>2</sub> O <sub>3</sub>	Minor2
Lead telluride oxide	Pb <sub>2</sub> TeO <sub>3</sub>	Minor2
Lead tin fluoride	PSnF <sub>6</sub>	Minor2
Phenacite, am	Ca <sub>2</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub>	Minor2
Promethium lead telluride	Pb <sub>2</sub> TeO <sub>3</sub>	Minor2
Zinc lead oxide	Pb <sub>2</sub> Zn <sub>2</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub>	Minor2
<b>Storage area bulk dust sample</b>		
Silica, am	PS	Major1
Isobornite	Ca <sub>2</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> B <sub>2</sub> S <sub>6</sub>	Major1
Quartzite	PSiO <sub>2</sub>	Major1
Plumbogummite	Pb <sub>2</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> (PO <sub>3</sub> OH) <sub>2</sub>	Major1
Unsubstituted mineral	Ca <sub>2</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> B <sub>2</sub> S <sub>6</sub>	Major1
Isobornite	Ca <sub>2</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> B <sub>2</sub> S <sub>6</sub>	Minor2
Hydroxylite	Pb <sub>2</sub> As <sub>2</sub> S <sub>6</sub>	Minor2
Kambite	Pb <sub>2</sub> As <sub>2</sub> S <sub>6</sub>	Minor2
Isobornite	Pb <sub>2</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> B <sub>2</sub> S <sub>6</sub>	Minor2
Phenacite, am	Ca <sub>2</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub>	Minor2
Diopside	PSiO <sub>2</sub>	Trace3
<b>Shelf and dry furnace dust samples</b>		
Silica, am	PS	Major1
Isodimorphite	Pb <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub>	Major1
Isodimorph carbonite	Pb <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub>	Major1
Lead chloride hydride	Pb <sub>2</sub> Cl <sub>2</sub> (OH) <sub>2</sub>	Minor2
Cadmium lead oxide	CaPb <sub>2</sub> O <sub>3</sub>	Minor2
Lead chloride bromide	Pb <sub>2</sub> Br <sub>2</sub> (OH) <sub>2</sub>	Minor2
Phenacite, am	Ca <sub>2</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub>	Minor2
Vandinite	Pb <sub>2</sub> VO <sub>4</sub> Cl <sub>2</sub>	Minor2

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blast furnace and dross area were combined into one sample group. Figure 1 shows that the bulk dust samples from three different locations within the plant reacted similarly to the Tessier extraction chemicals with little regard to plant location or dust mineralogy. This may be an indication of the pervasiveness of coarse-grained PbS and its contribution to the sedimented dusts throughout the plant. The solubility of lead compounds was very low in the exchangeable and mildly acidic steps (<7% in all of the smelter areas), with the reducible, oxidation, and residual steps of the extraction procedure being much more effective at dissolving the lead compounds. It is interesting to note that the reducible fraction was highest in the dusts produced in association with the dross and blast furnaces (54%). This may be due to the presence of complex metalloid oxide compounds with lead. Furthermore, the abundance of PbS in the dusts, although pervasive throughout the plant, was greater in the ore concentrate and sinter dusts. The concentration of PbS gradually decreases as the ore is sintered and roasted. It is also apparent from Figure 1 that the residual fraction decreases in relation to the area of the smelter where the bulk dust was collected, with 43%, 26%, and 8% of the total lead in the ore storage, sinter, and blast/dross, respectively, being extracted in this step of the procedure. The bulk dusts collected from the blast and dross furnace areas were more soluble than the bulk dusts collected from the ore storage and sinter areas.

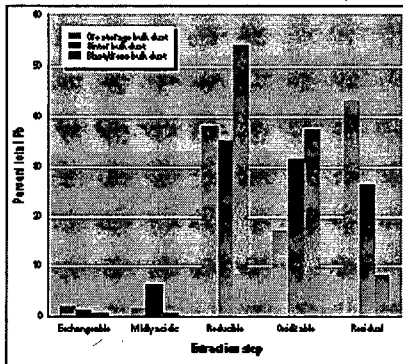


Figure 1. Percent total lead sequentially extracted from bulk dust by smelter process using the Tessier sequential extraction method (based on 0.50 g loose dust).

**Sequential extraction of airborne dusts.** The sequential extraction profiles for the airborne dust collected with the Andersen sampler from the different smelter processes are shown in Figures 2-5. The extraction profile for the ore-storage airborne dust samples, shown in Figure 2, indicates the sequential extraction of lead from the airborne dust was more effective for the finer particle sizes during the exchangeable and mildly acidic steps. Of the total lead on the Andersen stages 2-4 and 5-7, 32% and 39%, respectively, were exchangeable, compared to slightly more than 1% exchangeable lead for the coarser particles from stages 0-1. For the mildly acidic step, 6% and 19% of the total lead on the Andersen stages 2-4 and 5-7, respectively, were extracted, compared to less than 1% for stages 0-1. This may be a reflection of the coarser grain sizes of PbS particles which were derived from the ore.

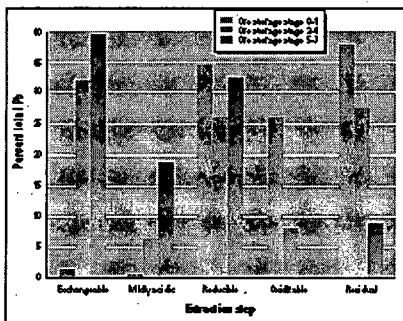


Figure 2. Percent total lead sequentially extracted by Andersen sampler stage from the ore-storage airborne dust samples.

A comparison between the bulk dust extraction profile shown in Figure 1 and the individual size fractions of dust from the ore storage Andersen samples, shown in Figure 2, indicates that the size fraction of the dust was an important factor in determining its solubility within the leach. The coarse fraction of the Andersen sampler (stages 0-1) most closely resembles the extraction profile of the ore storage bulk dust shown in Figure 1. This indicates that the extraction profile of the bulk dust was dominated by the coarser material within the dust and that the bulk of the lead resides within the coarse particle-size fraction of the dust from this area of the smelter. The extraction profile for the sinter airborne dust samples is shown in Figure 3. As with the ore storage air samples, the finer particles were consistently more soluble, and the extraction profile for the coarser particle fractions from the Andersen air samples most closely resembles the extraction profile of the sinter bulk dust shown in Figure 1.

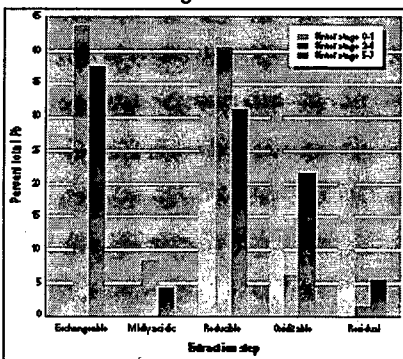


Figure 3. Percent total lead sequentially extracted by Andersen sampler stage from the sinter airborne dust samples.

Figure 4 shows the extraction profile for the combined airborne dust samples from the blast and dross furnaces. The highest percentages of total

lead were extracted during the first three steps of the extraction procedure. The total lead from the Andersen stages 0-1, 2-4, and 5-7, 67%, 44%, and 36%, respectively, were exchangeable. Figure 4 also suggests that the contribution of transient dust emanating from other areas of the smelter may misrepresent the dust actually produced in the blast and dross areas in that the airborne dust collected was much more soluble in the larger particle-size fractions than that indicated by the bulk dust extraction profile from this same area (see Figure 1). This may be explained by an examination of the volume and extraction percentages of lead in the airborne dust from the blast and dross furnace areas, shown in Figure 5. Although the coarse dusts sampled in the blast and dross furnace areas were very soluble, Figure 5 shows that the largest percentage of blast and dross lead collected with the Andersen sampler was associated with the very fine particle-size fractions from stages 5-7. From these stages, 24%, 15%, and 22% of the total lead were extracted during the exchangeable, mildly acidic, and reducible steps, respectively. This compares to 9%, 0.66%, and 1.4% of the total lead extracted from stages 0-1 during these same extraction steps. An analysis of the volume and extraction percentage of lead in the airborne dust from the ore storage area (not shown) revealed approximately 99% of the total lead collected with the Andersen sampler to be associated with the coarse particle fraction from stages 0-1. In addition, essentially all of the lead from the ore storage area was extracted during the reducible, oxidizable, and residual extraction steps.

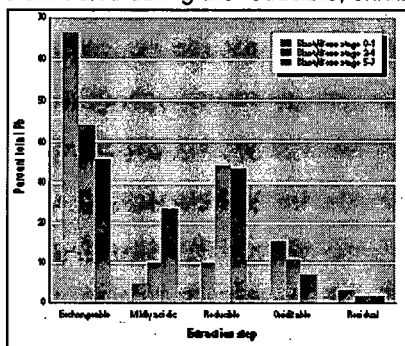


Figure 4. Percent total lead sequentially extracted by Andersen sampler stage from the combined blast and dross airborne dust samples.

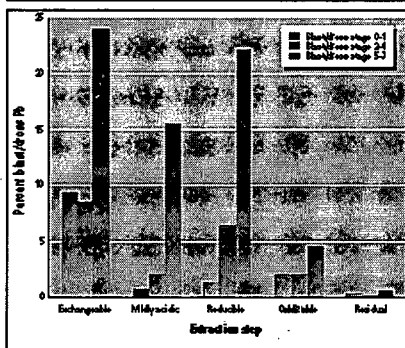


Figure 5. Percentage of the blast and dross lead sequentially extracted by Andersen sampler stage from the combined blast and dross airborne dust samples.

**Comparison with PbO-silica, PbSO<sub>4</sub>-silica, PbS-silica, and PbX-silica mixtures.** The distribution of a given metal between various fractions can only be considered as operationally defined by the method of extraction. To determine the solid phase solubility of lead compounds through the extraction scheme used in our study, a series of lead oxide (PbO), lead sulfate (PbSO<sub>4</sub>), and lead sulfide (PbS) mixtures with reagent-grade silica was prepared. The mixtures of reagent-grade PbO, PbSO<sub>4</sub>, and PbS powder with reagent-grade silica powder were mixed to approximately 16% total lead. The three PbX-silica mixtures were then blended into a fourth mixture containing 16% total lead, and all four mixtures were dissolved by the Tessier method.

Figure 6 depicts the extraction of lead for the individual steps of the extraction procedure on these mixtures. During the exchangeable step, 70 mg of the lead oxide was extracted, with 28 mg and 5 mg being extracted in the mildly acidic and reducible steps, respectively. The lead sulfate was only slightly less extractable during the exchangeable step (65 mg), with 53 mg and 18 mg being extracted in the mildly acidic and reducible steps, respectively. The lead sulfide was primarily extracted during the oxidation (58 mg) and residual (19 mg) steps. The mixture of lead compounds and silica appears to be a compromise of the other three compounds, with the lead oxide and lead sulfate extracted during the first three steps and the lead sulfide extracted during the oxidation and residual step.

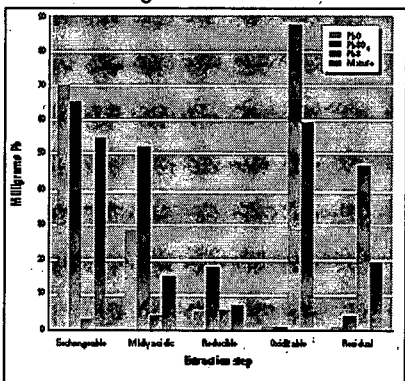


Figure 6. Milligrams of lead extracted from lead oxide-silica (PbO-SiO<sub>2</sub>), lead sulfate-silica (PbSO<sub>4</sub>-SiO<sub>2</sub>), lead sulfide-silica (PbS-SiO<sub>2</sub>) mixtures, and a composite mixture (PbX-SiO<sub>2</sub>) by the Tessier method.

### Concluding Remarks

In most workplaces, aerosol exposures involve the inhalation of many different types of particles that are distinguished not only by their size but also by their chemical, physical, and biological characteristics. The combined distributions of particle size and species together determine the

ability of the particles to reach given parts of the respiratory tract and their rate and intensity of action once they have arrived at the initial site of deposition. Currently, there is considerable interest in the various compounds that feature in aerosol exposure during the production and use of metals and in the setting of safe limits for their control. Whereas it is currently common practice to determine exposure in terms of the airborne concentration of the metal atoms that are present (e.g., by atomic absorption spectrophotometry), it is known that certain molecular forms are more harmful than others. In the production of nickel, for example, epidemiology has suggested that although water-soluble sulfidic and oxidic forms might be associated with lung and possibly nasal cancer, there is no such evidence for the metallic form (21). In such cases, the question of which chemical species is the most relevant to adverse health effects is therefore an important issue.

Our results of smelter lead dust speciation analysis for both the bulk dust samples and airborne dust samples confirmed that the lead dust mineralogy varies widely throughout the smelter, consisting of remnant sulfides and multimetal oxide phases. These findings are consistent with other studies that have reported galena as the major constituent in samples associated with ore handling, whereas lead oxide species ( $\text{PbO}_x$ ,  $\text{PbO} \cdot \text{PbSO}_4$ ) were the dominant species associated with smelter operations (9). Changes to the ore during the smelting process result in

changes to the mineralogy of the airborne dust, which are reflected in the Tessier sequential extraction method. Oxides and sulfates of lead are predominantly dissolved during the exchangeable and mildly acidic steps of the sequential extraction procedure, with lead sulfides and silicate minerals predominantly dissolved in the oxidizable and residual steps.

Dusts produced in the ore storage and sinter areas of the smelter are coarser and react later in the extraction steps than do the dusts produced in the blast and dross furnace areas. The dusts produced near these furnaces contain a higher percentage of soluble lead oxide, lead sulfate, and soluble lead. The finer particle sizes appear to be more soluble regardless of the bulk mineralogy of the dust. This finding is also in agreement with other studies (22). Assuming that the mobility and bioavailability of lead are related to its solubility as determined through sequential extraction, the health hazards from lead exposure may be appreciably enhanced in the blast and dross furnace processes. These areas have higher percentages of exchangeable lead and higher lead concentrations contained in the finer particle-size fractions.

This research has implications pertaining to lead exposure to residential districts near the smelter. Entrainment of soil particles is an important route of lead transport contributing to the atmospheric burden around lead smelting facilities. Large particles ( $d_{aa} > 2 \mu\text{m}$ ) emitted from the smelter settle out of the atmosphere fairly rapidly and are deposited relatively close to the smelter. These larger settled particles can become more bioavailable as they are ground into smaller particles within the home environment. The smaller and more bioavailable particles emitted from the smelter may be transported many kilometers from the smelter (23). Lead particles emitted from the smelter would be primarily in the form of lead sulfur compounds,  $\text{PbSO}_4$ ,  $\text{PbO} \cdot \text{PbSO}_4$ , and  $\text{PbS}$ .

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# SLAG—IRON AND STEEL

By Rustu S. Kalyoncu

Domestic survey data and tables were prepared by Robin C. Kaiser, statistical assistant.

As early as 350 B.C., the Greek philosopher-physician Aristode prescribed iron slags for healing wounds. In the ensuing centuries, a number of applications for iron and steel slags were found. However, it was not until the early 20th century, when the modern processes of iron and steel production were developed, that the commercial, large-scale use of iron and steel slags became economical.

The American Society of Testing and Materials (ASTM) (1999) defines blast furnace slag as "the non-metallic product consisting essentially of calcium silicates and other bases that is developed in a molten condition simultaneously with iron in a blast furnace." To the casual observer, one of the most striking features of an iron and steel plant is the site of a mountainous slag pile that presents a continuous display as ladle after ladle pours its incandescent load down the side in the endless accumulation of this waste product. Almost a century ago, the term waste product aptly described slag. Slag was considered to be essential in the production of iron, but once it served its purpose in refining the metal, it was strictly a nuisance with little or no use. The usefulness of slags was realized with the first ore smelting process. The use of slags became a common practice in Europe at the turn of the 19th century, where the incentive to make all possible use of industrial byproducts was strong and storage space for byproducts was lacking. Shortly after, many markets for slags opened in Europe, the United States, and elsewhere in the world.

In the production of iron, the blast furnace (BF) is charged with iron ore, fluxing agents (usually limestone and dolomite) and coke as fuel and the reducing agent. The iron ore is a mixture of iron oxides, silica, and alumina. From this and the added fluxing agents, alkaline earth carbonates, molten slag,

and iron are formed. Oxygen in the preheated air blown into the furnace combines with the carbon of the coke to produce the needed heat and carbon monoxide. At the same time, the iron ore is reduced to iron, mainly through the reaction of the carbon monoxide with the iron oxide to yield carbon dioxide ( $\text{CO}_2$ ) and metallic iron. The fluxing agents dissociate into calcium and magnesium oxides and carbon dioxide. The oxides of calcium and magnesium combine with silica and alumina to form slag. The slag is transported into a cooling pit either directly or via iron ladles, depending on the distance between the pit and the furnace.

The principal constituents of iron and steel slags are silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ), calcia ( $\text{CaO}$ ), and magnesia ( $\text{MgO}$ ), which make up 95% of the composition. Minor elements include manganese, iron, and sulfur compounds, as well as trace amounts of several others. The physical characteristics, such as density, porosity, and particle size, are affected by the cooling rates of the slag and its chemical composition. Depending on the cooling method, three types of BF slag are produced: air-cooled, expanded, and granulated.

Allowing the molten slag to cool slowly in air in an open pit produces air-cooled slag. Air-cooled blast furnace slag is defined in ASTM standard C-125 (American Society for Testing and Materials, 1999) as "the material resulting from solidification of molten blast furnace slag under atmospheric conditions. Subsequent cooling may be accelerated by application of water to the solidified surface." The solidified slag has a vesicular structure with closed pores. The rough vesicular texture of slag gives it a greater surface area than smoother aggregates of equal volume and provides an excellent bond with portland cement, as well as high stability in asphalt

## Slag—Iron and Steel in the 20th Century

Early use of blast furnace slag in the United States was prompted by the desire to make use of material that was considered an expensive waste product. Its use in earnest started in the early 1900s in the construction field, principally for railroad ballast, portland-cement-concrete aggregate, and aggregates for bituminous and other types of road construction. The National Slag Association carried out a survey of slag shipments in the United States for the first time in 1938. In 1939, the first year for which comprehensive figures of marketed slag are available, 8.3 million metric tons of blast furnace slag valued at \$6.4 million was used. The slag output from blast furnaces in 1947, the first year in which the U.S. Bureau of Mines collected production statistics, reached almost 30 million tons. Most slag was used in highway construction and railroad ballast.

In 2000, 8.9 million tons of blast furnace slag valued at \$58.3 million and 5.1 million tons of steel slag valued at \$20.1

million were used. Major uses were in road construction, asphaltic concrete aggregate, portland cement manufacture, and various concrete products. In the early years of slag use, prospective consumers thought that slag was subject to disintegration and corrosion and was brittle. Slag cements also were questioned, and slag wool was believed to have high sulfur content. Only after years of research and promotion were these objections overcome. In 2000, the ferrous slag industry enjoyed the benefits of many individual and collective efforts expended in the development of slag markets. A broader market existed for slag, from mineral wool to roofing granules to agriculture. Virtually all of the slag produced by the iron and steel industry throughout the world was used in such applications as asphaltic concrete aggregate, cement extenders, fill, railroad ballast, road bases, and roofing granules.

mixtures.

Expanded slag is formed through controlled rapid cooling of molten slag in water or in water with combination of steam and compressed air. Steam and other gases enhance the porosity and vesicular nature of the slag, resulting in a lightweight aggregate suitable for use in concrete. Quenching the molten slag into glass granules by using high-pressure water jets produces granulated slag. Quenching prevents the crystallization of minerals constituting the slag composition, thus resulting in a granular, glassy aggregate. This slag is crushed, pulverized, and screened for use in various applications, particularly in cement production, because of its pozzolanic (hydraulic cementitious) characteristics.

Slags are also coproducts of steelmaking processes. Production of steel calls for the removal of excess silicon by mineralization and of carbon by oxidation from pig or crude iron. Steel slag is a hard, dense material somewhat similar to air-cooled iron slag. It contains significant amounts of free iron, giving it its high density and hardness, which make it particularly suitable as a road construction aggregate.

Slag is transported to processing plants, where it undergoes crushing, grinding, and screening operations to meet various use specifications. Processed slag is either shipped to its buyer for immediate use or, in slack seasons, stored.

#### Legislation and Government Programs

Classification of slags under several standard waste categories has been the subject of a number of past Government initiatives. The National Slag Association reported no major Government action concerning slag in 2000 (R.Y. Twitmyer, President, National Slag Association, oral commun., 2000). The effect of increased spending on highway construction and repairs, as a result of the passage of the Transportation Equity Act for the 21st century (Public Law 105-178) by Congress in 1998, with its \$205 billion spending plan, did not show on the consumption and price of slags in 2000.

The Portland Cement Association is promoting slag use in portland cement production. The potential for a carbon tax levy on CO<sub>2</sub> emissions may provide the cement producers with incentives to find ways of reducing CO<sub>2</sub> emissions in portland cement production, where the burning fuel and decomposition of carbonates in the raw feed contribute to CO<sub>2</sub> emissions.

Texas Industries has developed a process for cement clinker production involving the use of steel slag. In this process, called CemStar, steel slag is fed into the rotary kiln as a part of the raw meal. Replacing a part of the raw meal directly with slag will result in the lowering of CO<sub>2</sub> emissions directly proportional to the quantities of slag used. Additional refinements of the process have been reported (Robert D. Rogers, President, Texas Industries, oral commun., 2000).

#### Production

The iron and steel industry does not routinely measure slag output; therefore, actual annual ferrous slag production data in the United States do not exist. The data collected by the U.S. Geological Survey (USGS) reflect the slag processing industry's sales rather than the output. Slag outputs in iron and steel production are highly variable and depend, partly, on the composition of the raw materials and the type of furnace. Typically, for ore feed with 60% to 65% iron, blast furnace slag production ranges from about 220 to 370 kilograms per metric ton of pig iron produced. Lower grade ores yield much higher

slag fractions, sometimes as high as 1 ton of slag per ton of pig iron. Steel slag outputs are approximately 20% by mass of the steel output. About one-half of the slag is entrained steel, which is generally recovered and returned to the furnace. After removal of the entrained steel, the marketable slag is equivalent to about 10% to 15% of the original steel output.

According to statistics reported by the American Iron and Steel Institute, U.S. pig iron production was about 46 million tons (Mt) and 48 Mt in 1999 and 2000, respectively. The iron slag production figures for these years were about 11.5 Mt and 12 Mt in 1999 and 2000, respectively. Similarly, U.S. steel production was reported to be 97 Mt for 1999 and 101 Mt for 2000. The expected steel slag production was about 11 Mt for 1999 and 13 Mt in 2000. As with the United States, no data are available on world slag production. The International Iron and Steel Institute (2000, p. MM16) reported the world pig iron output to be about 570 Mt and crude steel production to be 828 Mt in 2000. The estimated figures for ferrous slag production from this output was approximately 200 Mt.

Tables 1 through 8 list data compiled from the USGS survey of domestic slag processors. The data for 1999 and 2000 reflect a response by 90% of the processors queried. Where applicable, estimates have been incorporated for data omitted from the returned questionnaires. Table 8 lists the production facilities that responded to the survey in 2000. Redland Mill Services no longer appears in the table because Lafarge Corp. bought it 2 years ago.

Nucor Corporation's new 1-million-ton-per-year electric-arc furnace steel mill in Hertford County, NC, the construction of which was started in 1998 (Kalyoncu, 1999), became operational in October 2000 (Giff Daughtridge, plant manager, Nucor Plant, oral commun., 2001). Currently [2000], the mill is operating at 70% capacity and generating approximately 25,000 tons of slag, which is processed by Heckett MultiServ Co.

GSC Partners is in the process of acquiring Envirosource (R.Y. Twitmyer, National Slag Association, oral commun., 2001).

#### Consumption

Uses of iron and steel slags range from building and road construction to waste stabilization. Iron and steel slags are also used in cement manufacture, concrete aggregates, agricultural fill, glass manufacture, and as a mineral supplement and liming agent in soil amendment. The correlation between slag production and availability is not a good indicator of consumption trends because time lags between production and sale of the slag to the final customer can be significant. The primary reason for the lag is the necessity of aging the new slag to reduce its free-lime content for certain applications, such as concrete production. High levels of free lime can adversely affect concrete performance. Generally, slag, especially steel slag, will be stored to cure for 6 months or longer to allow expansion of dicalcium silicate and to reduce the free-lime content to acceptable levels. Furthermore, many slag producers accumulate large stockpiles to be able to participate in bids to supply large construction projects.

Air-cooled slag accounted for the bulk of slag production (sales) in the United States. The total U.S. sales of about 9 Mt, worth more than \$59 million, of domestically produced air-cooled blast furnace slag recorded a slight increase in value (table 1). Expanded and granulated slag sales increased. Total revenues of more than \$141 million (iron plus steel slags) for

2000 were slightly higher than those of 1999. The mid-Atlantic region, for a second year, remained the leader in sales value of blast furnace slag with \$55 million, accounting for more than 45% of total revenues for the whole country, with the north-central region accounting for most of the remaining business (table 3).

In 2000, sales for concrete and asphaltic road construction, including road base, again accounted for more than three quarters of the consumption of air-cooled BF slags in the United States; other uses were in soil conditioning, sewage treatment, and mineral wool production (table 4).

Road base was the primary use of steel slag, followed by fill and asphaltic concrete aggregates. The steel slag sales of \$20.1 million in 2000 lagged behind the 1999 figure of \$23 million by almost 13% (table 5). Slag prices showed a range of values depending on their use categories (table 6). A significant amount of slag, 2.4 Mt, was never shipped but used at the plants (table 7).

In 2000, the United States imported 1.5 Mt of ferrous slags. Granulated blast furnace slag (GGBFS), which commands the highest price among ferrous slags, led the imports. In 2000, approximately 1 Mt of GGBFS was imported. Imports of GGBFS, in descending order, were mainly from Italy, Canada, France, South Africa, and Brazil. Principal discharge ports were Tampa, FL, New Orleans, LA, Philadelphia, PA, and Detroit, MI. In 2000, imports accounted for about 5% of total ferrous slag shipments in the United States.

#### Transportation

Most of the of ferrous slag sold and not consumed at the plant was transported by truck; rail and barge transportation accounted for 21.5% of the total (table 7). Most ferrous slag was transported less than 100 kilometers; trucks were the most economical means of transportation for such distances.

#### Current Research and Technology

No significant developments were made in slag processing

technology during 2000. Because slag is a low unit-value, high-volume commodity, and slag processing is an established, conservative industry, all the slag that is processed is readily sold. Therefore, the industry seldom feels the need for innovations and, therefore, invests little, if any, in expensive research efforts. Previously reported advancements in granulating techniques (Kalyoncu, 1999) resulted in some improvements in slag granulation systems, especially in reducing the energy costs.

#### Outlook

Potential classification by the U.S. Environmental Protection Agency of iron and steel slags as hazardous wastes is of constant concern to the slag industry. Absent such a classification, ferrous slag has a secure future in the construction industry. Some blast furnace operations, however, have been closing because of an inability to compete in the marketplace. In the case of continuing plant closings, availability of domestic blast furnace slag may decline, which may necessitate an increase in imports. With its more limited uses, the long-term supply of steel slag appears to be more stable. An increase in the use of steel slags may be on the horizon as blast furnace slag production declines.

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- American Society for Testing and Materials, 1999, Standard terminology relating to concrete and concrete materials: West Conshohocken, PA, American Society for Testing and Materials, 4 p.
- International Iron and Steel Institute, 2000, Steel statistical yearbook: Brussels, International Iron and Steel Institute, 112 p.
- Kalyoncu, R.S., 1999, Slag—Iron and steel: U.S. Geological Survey Mineral Commodity Summaries 1999, p. 94-95.

#### U.S. Geological Survey Publications

- Iron and Steel. Ch. in Mineral Commodity Summaries, annual.
- Slag—Iron and Steel. Ch. in Mineral Commodity Summaries, annual.

TABLE 1  
IRON AND STEEL SLAG SOLD OR USED IN THE UNITED STATES 1/ 2/

(Million metric tons and million dollars)

Year	Blast furnace slag						Steel slag		Total slag	
	Air-cooled		Expanded 3/		Total		Quantity	Value 4/	Quantity	Value
1999	8.9	58.30	1.9	62.20	10.8 r/	120.00	6.2 r/	23.00 r/	17.1 r/	140.40 r/
2000	8.9	58.60	2.3	62.40	11.2	121.00	5.1	20.10	16.3	141.20

r/ Revised.

1/ Data are rounded to no more than three significant digits; may not add to totals shown.

2/ Excludes imported slag.

3/ Includes granulated slag to avoid disclosing company proprietary data.

4/ Value is the selling price at plant and includes, for a few facilities, estimates reported by the plants and/or made by the U.S. Geological Survey.

TABLE 2  
AVERAGE VALUE AT THE PLANT FOR IRON AND STEEL SLAG SOLD  
OR USED IN THE UNITED STATES, BY TYPE

(Dollars per metric ton)

Year	Iron blast furnace slag			Steel slag	Total slag
	Air-cooled	Expanded 1/	Total iron slag		
1999	6.50	32.00	11.00	3.92 r/	8.78 r/
2000	6.61	27.21	10.80	3.92	8.62

r/ Revised.

1/ Includes granulated slag to avoid disclosing company proprietary data.

TABLE 3  
BLAST FURNACE SLAG SOLD OR USED IN THE UNITED STATES, BY REGION AND STATE 1/ 2/

(Million metric tons and million dollars)

Region and State	1999				2000			
	Air-cooled		Total, all types		Air-cooled		Total, all types	
	Quantity	Value 3/	Quantity	Value 3/	Quantity	Value 3/	Quantity	Value 3/
North-Central: Illinois, Indiana, Michigan, Ohio	5.3	34.80	6.3	53.60	4.9	32.00	5.8	50.00
Mid-Atlantic: Maryland, New York, Pennsylvania, West Virginia	1.9	13.30	2.8	56.80	2.1	15.60	3.2	55.00
Other 4/	1.8	10.10	1.8	10.10	1.9	11.20	2.2	16.00
Total	8.9	58.30	10.9	120.00	8.9	58.60	11.2	121.00

1/ Data are rounded to no more than three significant digits; may not add to totals shown.

2/ Excludes imported slag.

3/ Value based on selling price at plant.

4/ Includes Alabama, California, Kentucky, Mississippi, and Utah.

TABLE 4  
AIR-COOLED BLAST FURNACE SLAG SOLD OR USED IN THE UNITED STATES, BY USE 1/ 2/

(Million metric tons and million dollars)

Use	1999		2000	
	Quantity	Value 3/	Quantity	Value 3/
Asphaltic concrete aggregate	1.7	11.30	1.7	11.30
Concrete aggregate	1.2	8.60	1.2	8.70
Concrete products	0.3	1.70	0.2	1.50
Fill	1.1	5.20	0.8	3.90
Mineral wool	0.5	4.40	0.5	5.00
Railroad ballast	0.2	0.60	(4/)	(4/)
Road bases	3.0	16.70	3.3	18.40
Roofing, built-up and shingles	(4/)	0.50	(4/)	(4/)
Other 5/	1.0	9.30	1.2	9.80
Total	8.9	58.30	8.9	58.60

See footnotes at end of table.

TABLE 4--Continued  
AIR-COOLED BLAST FURNACE SLAG SOLD OR USED IN THE UNITED STATES, BY USE 1/ 2/

- 1/ Data are rounded to no more than three significant digits; may not add to totals shown.  
2/ Excludes imports.  
3/ Value based on selling price at plant.  
4/ Less than 1/2 unit.  
5/ Includes cement, ice control, glass manufacture, sewage treatment, soil conditioning, and miscellaneous.

TABLE 5  
STEEL SLAG SOLD OR USED IN THE UNITED STATES, BY USE 1/ 2/ 3/

(Million tons and million dollars)

Use	1999 r/		2000	
	Quantity	Value 4/	Quantity	Value 4/
Asphaltic concrete aggregate	1.0	5.30	0.9	5.00
Fill	1.0	3.40	1.0	3.00
Railroad ballast	1.2	0.30	0.4	1.10
Road bases	1.8	6.02	1.7	6.30
Other 5/	1.2	8.00	1.1	4.70
Total	6.2	23.00	5.1	20.10

r/ Revised.

1/ Data are rounded to no more than three significant digits; may not add to totals shown.

2/ Excludes imports.

3/ Excludes tonnage returned to furnace for charge material.

4/ Value based on selling price at plant.

5/ Includes ice control, soil conditioning, and miscellaneous uses.

TABLE 6  
AVERAGE AND RANGE OF SELLING PRICES AT THE PLANT FOR IRON AND STEEL SLAG IN THE UNITED STATES IN 2000, BY USE

(Dollars per metric ton)

Use	Iron blast furnace slag 1/		Steel slag	
	Average	Range	Average	Range
Asphaltic concrete aggregate	5.00	4.00-8.00	4.00	2.00-8.00
Concrete products	5.00	3.30-8.00	(2/)	(2/)
Fill	4.00	2.00-9.00	2.00	0.99-14.00
Mineral wool	7.00	4.00-10.00	W	(2/)
Railroad ballast	4.00	3.00-8.00	2.00	2.00-3.00
Road bases	5.00	1.00-8.00	3.00	2.00-12.00
Roofing, built-up and shingles	11.00	6.00-14.00	(2/)	(2/)
Other 3/	7.00	6.00-79.00	5.00	4.00-8.00

W Withheld to avoid disclosing company proprietary information.

1/ Air-cooled slag only. Price range breakouts, by use, for granulated and expanded slag are withheld to avoid disclosing proprietary information; overall, prices ranged from \$2.00 to \$8.00 per metric ton for iron and steel slag.

2/ No use reported.

3/ Includes cement manufacture, glass manufacture, sewage treatment, and soil conditioning.

TABLE 7  
SHIPMENTS OF IRON AND STEEL SLAG IN THE UNITED STATES IN 2000,  
BY METHOD OF TRANSPORTATION 1/ 2/

(Million metric tons)

Method of transportation	Quantity
Truck	10.9
Rail	0.8
Waterway	2.2
Total	13.9
Not transported (used at plant)	2.4

1/ Data are rounded to no more than three significant digits; may not add to totals shown.

2/ Excludes imported slag.



TABLE 8  
PROCESSORS OF IRON AND STEEL SLAG IN THE UNITED STATES IN 2000

Company	Plant location	Steel slag			Iron slag	
		Basic oxygen furnace	Open hearth	Electric arc furnace	Blast furnace	Slag type
Blue Circle Cement Co.	Baltimore, MD	X			X	Granulated.
Buffalo Crushed Stone, Inc.	Buffalo, NY	X			X	Air cooled.
C.J. Langenfelder	Baltimore, MD	X				
Do.	Braddock, PA	X				
Edward C. Levy Co.	Detroit, MI	X		X	X	Air cooled and expanded.
Heckett MultiServ Co.	Armored, AR			X		
Do.	Fontana, CA	X			X	Air cooled.
Do.	Wilton, IA			X		
Do.	Chicago, IL			X		
Do.	Sterling, IL			X		
Do.	East Chicago, IN	X				
Do.	Indiana Harbor, IN	X				
Do.	Ashland, KY	X			X	Air cooled.
Do.	Coalton, KY			X		
Do.	Newport, KY			X		
Do.	Owensboro, KY			X		
Do.	Kansas City, MO			X		
Do.	Canton, OH			X		
Do.	Mansfield, OH	X				
Do.	Massillon, OH			X		
Do. (Warren Plant)	Warren, OH	X				
Do.	do.			X		
Do.	Youngstown, OH			X		
Do.	Butler, PA			X		
Do.	Provo, UT		X		X	Air cooled.
International Mill Services	Fort Smith, AR			X		
Do.	Kingman, AZ			X		
Do.	Pueblo, CO	X				
Do.	Claymont, DE			X		
Do.	Cartersville, GA			X		
Do.	Alton, IL			X		
Do.	Chicago, IL			X	X	Air cooled.
Do.	Kankakee, IL			X		
Do.	Gary, IN			X		
Do.	Huntington, IN			X		
Do.	Laplace, LA			X		
Do.	Jackson, MI			X		
Do.	Monroe, MI			X		
Do.	St. Paul, MN			X		
Do.	Jackson, MS			X		
Do.	Charlotte, NC			X		
Do.	Perth Amboy, NJ			X		
Do.	Riverton, NJ			X		
Do.	Sayreville, NJ			X		
Do.	Auburn, NY			X		
Do.	Hubbard, OH			X		
Do.	Marion, OH			X		
Do.	Mingo Junction, OH	X		X		
Do.	Warrent, OH			X		
Do.	McMinnville, OR			X		
Do.	Portland, OR			X		
Do.	Brideville, PA			X		
Do.	Coatesville, PA			X		
Do.	Holsopple, PA			X		
Do.	Houston, PA			X		
Do.	New Castle, PA			X		
Do.	Midland, PA			X		
Do.	Pricedale, PA	X		X		
Do.	Reading, PA	X		X		
Do.	Darlington, SC	X		X		
Do.	Georgetown, SC	X		X		
Do.	Jackson, TN	X		X		
Do.	Beaumont, TX	X		X		

TABLE 8--Continued  
PROCESSORS OF IRON AND STEEL SLAG IN THE UNITED STATES IN 2000

Company	Plant location	Steel slag			Iron slag	
		Basic oxygen furnace	Open hearth	Electric arc furnace	Blast furnace	Slag type
International Mill Services--Continued:	El Paso, TX	X		X		
Do.	Jewett, TX	X		X		
Do.	Longview, TX	X		X		
Do.	Plymouth, UT	X		X		
Do.	Seattle, WA	X		X		
Do.	Saukville, WI	X		X		
Do.	Weirton, WV	X		X		
Holnam Inc.	Gary, IN				X	Air cooled, granulated, and expanded.
Do.	Weirton, WV				X	Granulated.
IMS Waylite Corp.	Bethlehem, PA	X	X		X	Air cooled and expanded.
Do.	Cambria, PA		X		X	Air cooled.
Lafarge Corp.	Cuyahoga, OH		X			do
Do.	Lordstown, OH		X		X	Granulated.
Do.	McDonald, OH		X			
Do.	Mingo Junction, OH				X	Air cooled.
Do.	Warren, OH				X	do.
Do.	Youngstown, OH		X			
Do.	West Mifflin, PA				X	do.
Do.	Weirton, WV				X	do.
The Levy Co. Inc.	Burns Harbor, IN	X			X	do.
Do.	East Chicago, IN				X	do.
Martin Marietta Aggregates	Raleigh, NC	X			X	do.
Maryland Slag Co.	Baltimore, MD				X	do.
Olympic Mill Services	Seguin, TX			X		
Stein, Inc.	Decatur, AL	X				
Do.	Cleveland, OH	X			X	do.
Do.	Lorain, OH				X	do.
Vulcan Materials Co.	Alabama City, AL				X	do.
Do.	Fairfield, AL	X			X	do.



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## Lead > Secondary Lead Smelter eTool

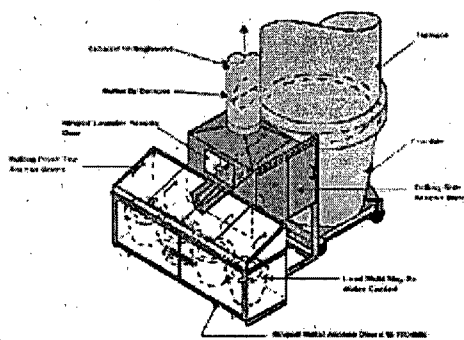
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### Smelting > Blast Furnace

Blast furnaces are designed and operated to produce a hard (high alloy content) lead product. Blast furnaces emit high levels of lead fume during the the following processes:

- o [Charging](#)
- o [Tapping](#)
- o [Tuyere Punching](#)

- ▶ [Cross-sectional view of blast furnace](#)
- ▶ [Additional blast furnace images](#)



Click for larger view of blast furnace lead tap controls diagram

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[Smelting](#)

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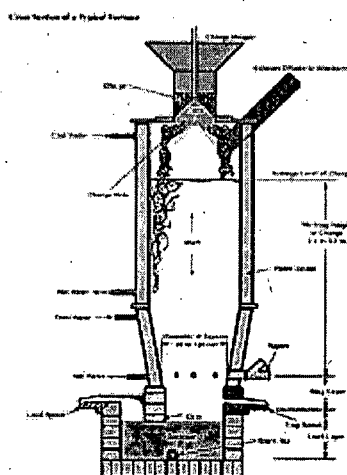
### Charging

#### Potential Sources of Exposure:

- o Spillage or emissions may occur at blast furnace feed conveyor transfer points and charging points.
- o Spillage of lead-containing dust may occur if bucket elevators, conveyors, or skip hoists are overfilled.
- o Lead fume and dust may be emitted from the blast furnace if the charge level is too low.

#### Possible Engineering and Work Practice Controls:

- o Maintain raw material storage and handling areas under negative pressure to prevent contamination of adjacent work areas.
- o Prevent puffing by providing and maintaining process controls to ensure that the proper amount of charge material is in the thimble on the top of the



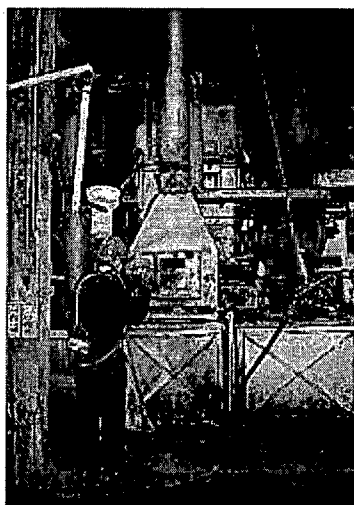
Click for larger view of blast furnace diagram

furnace.

- o Provide hooding with sufficient exhaust ventilation at furnace feed conveyor loading and charge points to capture dusts and fumes which may be emitted.
- o Provide hooding with sufficient exhaust ventilation to capture dusts which may be generated when charging the furnace.
- o Do not overfill bucket elevators, conveyors, or skip hoists.
- o Maintain positive-pressure, HEPA filtered air systems on mobile equipment to ensure effective operation. Check and change air filters regularly as part of an effective scheduled preventative maintenance program.
- o Vacuum any spills immediately with a HEPA filtered vacuum system. Water should not be used in the smelting area for dust suppression due to the possibility of oxide fires and the mixing of water and molten lead.

### Tapping

Blast furnace tapping operations involve removing the slag and then tapping molten lead from the furnace into molds or ladles. Some smelters tap metal directly into a holding kettle which keeps the metal molten for refining. The other smelters cast the furnace metal into blocks and allow the blocks to solidify.



Slag tap with enclosure hooding and local exhaust ventilation

### Potential Sources of Exposure:

- o Lead fumes may be emitted at the lead or slag tapping plugs during removal of the tapping plug or while lancing the tapping plug.
- o Emissions may occur while pouring lead or slag at the tapping launder, mold, ladle, or refining kettle.
- o Lead dust may become airborne due to disturbance of settled dust in the smelting area.
- o Emissions may occur from ladles containing slag or molten lead.
- o Spilled slag or molten lead may emit lead fumes.

### Possible Engineering and Work Practice Controls:

- o Provide local exhaust ventilation at the lead and slag tap, launders, molds,

ladles, and refining kettles.

► [Blast Furnace Lead Tap Controls Diagram](#)

► [Blast Furnace Slag Tap Controls Diagram](#)

- o Allow lead and slag pots to remain under the exhaust hood until crusted to minimize fume emissions.

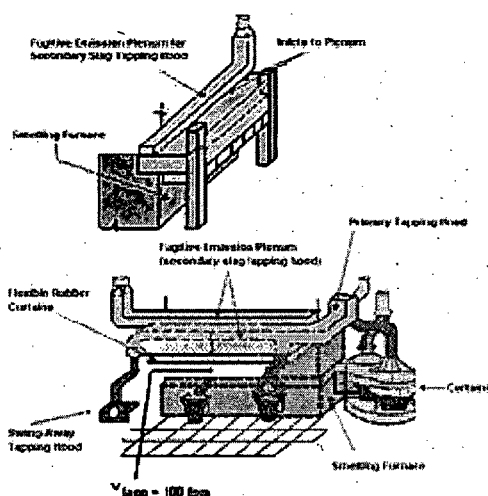
► [Secondary Exhaust Hood Diagram](#)

- o Provide a supplied air island at lead and slag tapping stations.

► [Supplied Air Island Diagram](#)

- o Provide local exhaust ventilation for staged slag pots if necessary.

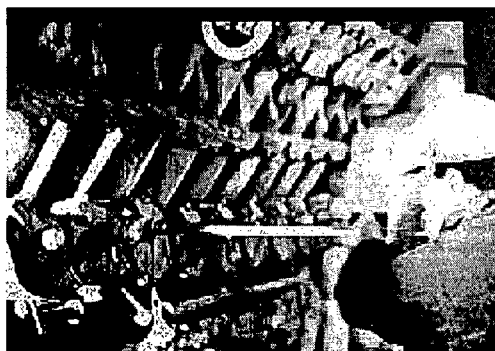
► [Moveable Exhaust Hood Diagram](#)



Click for larger view of secondary exhaust hood diagram

### Tuyere Punching

Blast air for the combustion process enters the blast furnace through "tuyeres." The tuyeres occasionally begin to fill with accretions and must be physically punched, usually with a steel rod, to keep them unobstructed. The conventional method used for this task is to remove the cover of the tuyeres and insert the steel rod. After the accretions have been "punched," the cover is replaced.



Manual tuyere punching

Recently smelters have been able to adapt an "off-the-shelf" automatic tuyere puncher that has greatly reduced employee lead exposure. However, even with the automatic system there are occasions when the tuyere pipe has to be cleared by using a jackhammer or rod.

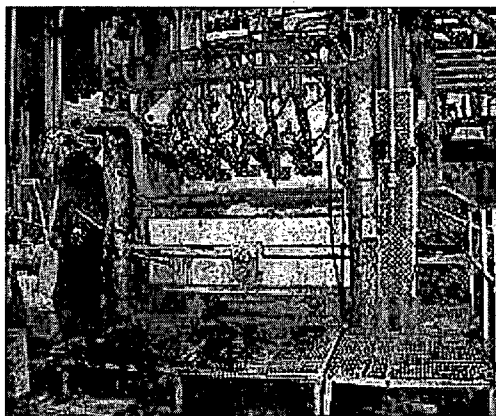
### Potential Sources of Exposure:

- o Significant lead fume emissions may come from the furnace during manual punching.

### Possible Engineering and Work Practice Controls:

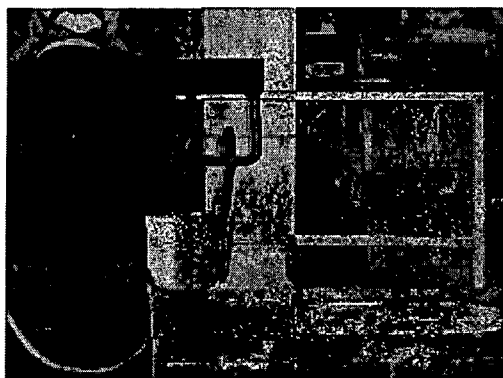
- o Provide automatic tuyere punching.
  - [Hydraulic Tuyere Punch Diagram](#)
- o Use notched, rotating tuyere covers to minimize tuyere opening during punching.

- o Stand to the side of the tuyere when opening the cover during the tuyere punching operation.
- o Provide a rod of sufficient length to minimize operator exposure.
- o Provide a viewing port on the tuyere cover so that plugging can be observed without removing the cover.

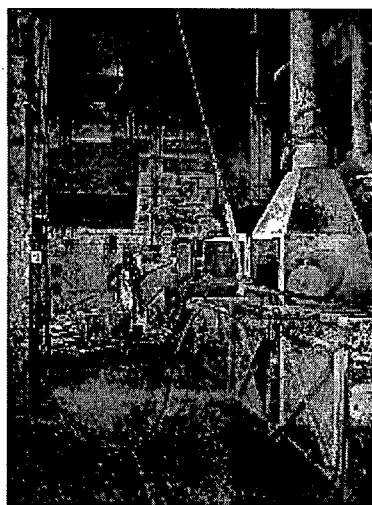


Automatic tuyere puncher

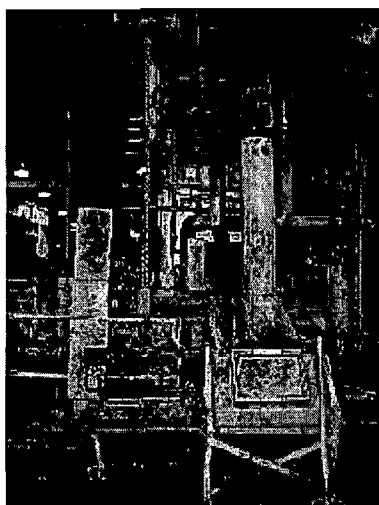
#### Additional Images



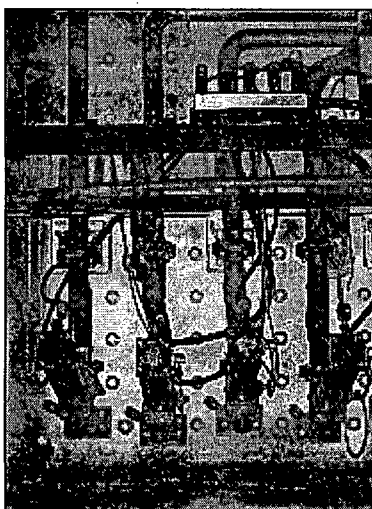
Lifting recently cast lead blocks from mold



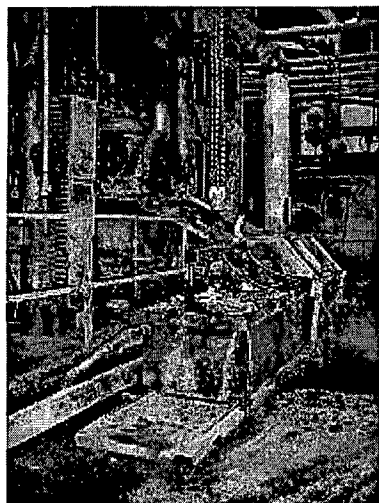
Slag side of blast furnace



Local exhaust ventilation at lead tap



Automatic tuyere punch



Liquid lead cooling in molds



Lead flowing into mold

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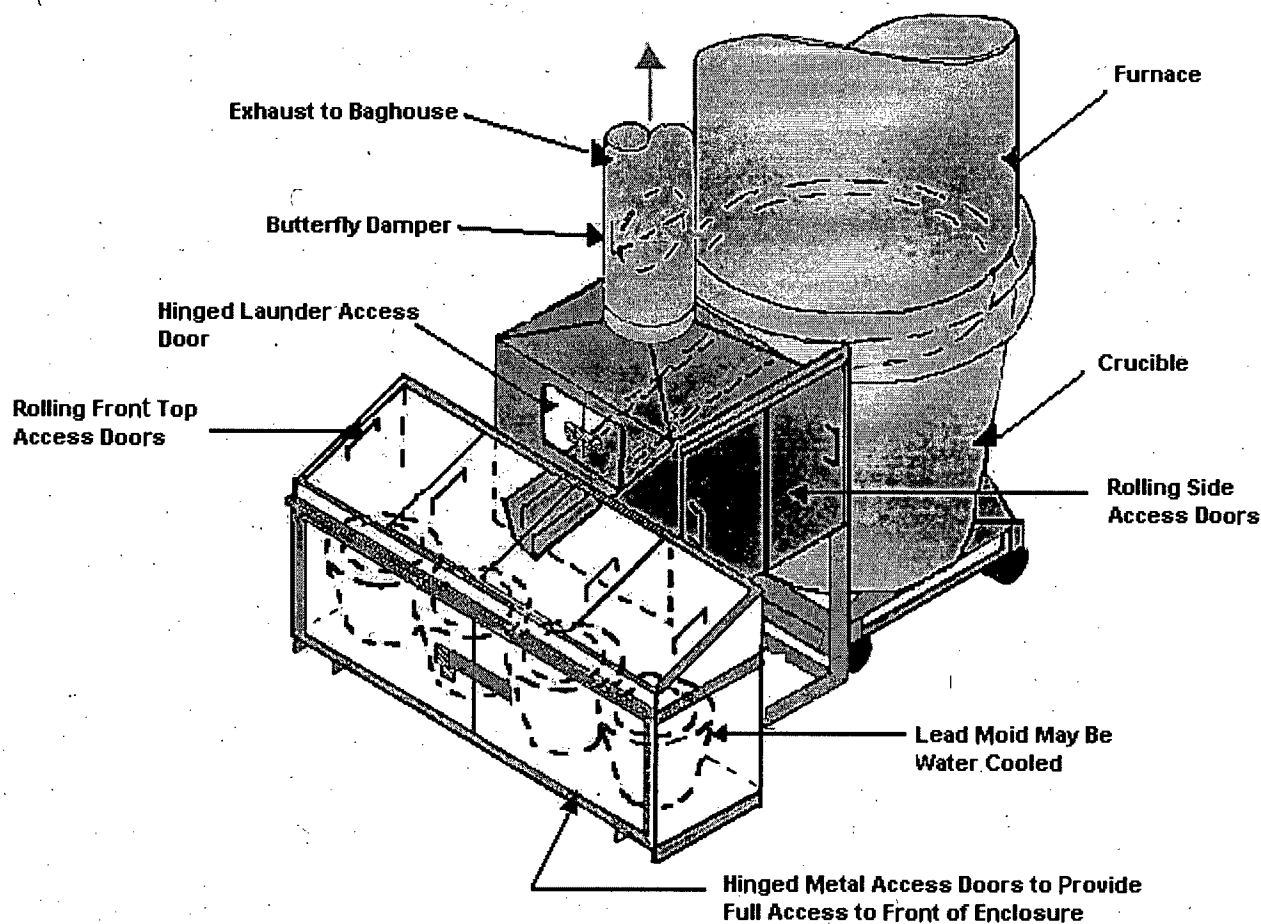
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## Enclosure Hooding - Furnace Lead Tap Controls



### Design Characteristics

- o Enclosure to provide capture velocities at opening of 350-500 FPM
- o Transport velocity in ducts greater than or equal to 4000 FPM





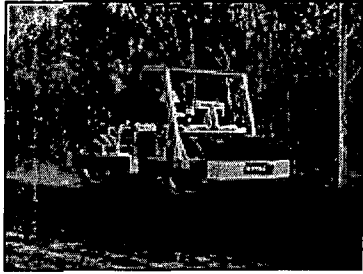
# National Slag Association

Founded in 1918

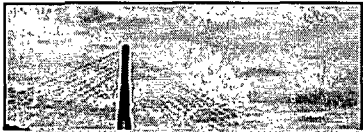
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## Common uses for slag

Blast Furnace Slag			Steel Slag
Air-Cooled	Pelletized	Granulated	
Asphalt aggregate	Concrete masonry	GGBS cement	Asphalt aggregate
Concrete/Masonry aggregate	Lightweight concrete	Soil cement	Fill
Insulation/mineral wool	Lightweight fill	Roller compacted concrete	Cement Mfg. raw feed
Cement Mfg. raw feed	Insulation		Agriculture/Soil Amendment
Agriculture/Soil Amendment	Road Base	Road Base	Environmental Applications
Fill	✱	Agriculture/Soil Amendment	Railroad ballast
Roof aggregate	✱	✱	Road Base
Railroad ballast	✱	✱	Gabions/Rip Rap
Glass manufacture	✱	✱	✱
Environmental Applications	✱	✱	✱
Gabions/Rip Rap	✱	✱	✱



The use of steel slag as an aggregate is considered a standard practice in many jurisdictions, with applications that include its use in granular base, embankments, engineered fill, highway shoulders, and hot mix asphalt pavement.



**"The AGGREGAT of Choice for Building Green"**

# NATIONAL SLAG ASSOCIATION



## LEACHATE FROM BLAST FURNACE SLAG - What it is and How to treat it

The following is a brief description of Blast Furnace Slag chemistry and the phenomenon of leaching as it relates to this material.

### BLAST FURNACE SLAG - Defined

Blast Furnace Slag is defined as the non-metallic product consisting essentially of silicates and alumino-silicates of calcium and other bases that is developed in the molten condition simultaneously with iron in a blast furnace. The blast furnace is the primary means for reducing iron oxides to molten, metallic iron. Molten iron collects at the bottom of the blast furnace and the liquid slag floats on it. Periodically both are tapped from the furnace, with the slag being solidified and recycled for use in a variety of markets; including construction aggregates, GGBS cement, glass, and as a substitute for natural materials.

Typical Air-Cooled Blast Furnace slag chemistry is as follows:

<u>CONSTITUENT</u>	<u>PERCENT by WEIGHT</u>
Calcium Oxide (CaO)	32 to 45
Magnesia (MgO)	5 to 15
Silica (SiO <sub>2</sub> )	32 to 42
Alumina (Al <sub>2</sub> O <sub>3</sub> )	7 to 16
Sulfur (S)	1 to 2
Iron Oxide (Fe <sub>2</sub> O <sub>3</sub> )	0.1 to 1.5
Manganese Oxide (MnO)	0.2 to 1.0

These constituents usually exist as an isomorphous mixture with the following general formula:



This formula represents the Melillite mineral series.

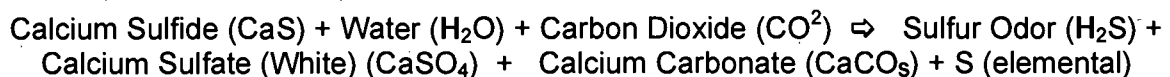
## **LEACHATE – What it is, How to treat it**

Leachate can be described as a solution or product that is obtained when a solid material has been extracted or dissolved by the action of a percolating liquid (water). Whenever water comes in direct contact with a solid material, the potential for leachate to form exists.

Typically leaching is an aesthetic issue and not harmful to the environment.

The potential for leaching is source specific. Several methods have been developed to limit the potential for leaching. These include treating slag with: hydrogen peroxide, permanganate (potassium or sodium), hypochlorite or aging. If leaching does occur, remediation can be accomplished by dilution, containment of the leachate and removal by vacuuming, or natural oxidation, all of which can be effective.

### **TYPICAL CHEMICAL PROGRESSION**



The rate of leaching diminishes rapidly with time and as the chemical nature of the sulfur products change from sulfide to sulfate by aging (oxidation). Although no exact timetable for this process has been established, most leachate events are of short duration and are a one time occurrence. The occurrence of Blast Furnace slag leachate, while uncommon, is irritating to those nearby due to the odor. Fortunately, its long-term impact on the environment appears minimal. An Environmental Impact Study by the Army Corps of Engineers (Bethlehem Steel, Sparrows Point, PA) has stated that little, if any, environmental damage is to be expected to the existing eco-system due to the presence of slag in an aquatic environment. A Risk Assessment Study on iron and steel slag is available from the National Slag Association.

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## **IRON and STEEL SLAGS - - NON-HAZARDS**

### **A Special Report from the National Slag Association**

Allegations of iron and steel making slags being "hazardous" are the subject of numerous files in the National Slag Association office dating back to the 1920's.

### **Federal Register Explanation**

The Federal Register, Vol. 45, No. 98, May 19, 1980, lists the substances ruled hazardous by EPA. On page 33124, four steel-industry substances were listed. These were identified to EPA by a consulting firm requested to examine all steel-industry products, including slag, to determine which were hazardous under EPA criteria. Slag was tested by EPA standards and found to be non-hazardous.

Don Lewis, Chief Engineer of NSA, described this in a December 14, 1980 letter:

"The original EPA proposed regulation for hazardous wastes contained three items that could have resulted in slags being covered by that regulation, despite statements by EPA personnel that they did not intend for steel-industry slags to be so classified. These were: (1) retained heat that could ignite fires, (2) a limit of 12 pH on leachates that would be classified as "corrosive" and (3) classification as "reactive" of cyanide or sulfide-bearing materials that could generate toxic gases when exposed to either acid or alkaline conditions. There was also a possibility that some slags would be borderline on toxicity when acid leaching was used with limits of 10 times drinking water standards.

"Both the American Iron and Steel Institute and the National Slag Association submitted formal comments to EPA, objecting to these provisions on the basis that slags are not hazardous but could be placed in that category by improper definitions or requirements. All of these objections were considered by EPA, and suitable changes were made in the final regulation published in Part III of the Federal Register for Monday, May 19, 1980.

"EPA's own contact research studies listed slags as non-hazardous under the existing test methods and standards; a fact that undoubtedly helped in the consideration of our comments.

"The criteria for hazardous waste classification in the Federal Register of May 19, 1980 cover four major characteristics: Ignitability, Corrosivity, Reactivity, and Toxicity. As explained on pages 33108 and 33109, retained heat from manufacturing or processing was dropped from the standard to avoid inclusion of slags in the Ignitability hazard class.

"Corrosivity requirements were changed to only include liquid wastes and the upper pH value raised to 12.5 or more, effectively excluding high pH steel slag from the hazardous classification. The reactivity standards, as noted on pages 22110, were revised to require that any toxic gases generated must be in 'a quantity sufficient to present a danger to human health or the environment'; slag generating only minute quantities are, therefore, exempted. The Toxicity requirements set maximum leachate values at 100 times the drinking water standard, far higher than any slag could ever be expected to test.

"Known or suspected toxic wastes were listed in sections 261.31 and 261.32 of the standard (pages 33123 and 33124). 'Dewatered air pollution control scrubber sludges from coke oven and blast furnaces' were listed in 261.31 as hazardous waste number F016. In 261.32, four steel-industry wastes were listed under number K060 to K063, inclusive. Only one of these, K061 - Emission control dust/sludge from the electric furnace production of steel, is the only one related to furnace operation.

"In the final listing of Hazardous Wastes, Part VII, Federal Register for Wednesday, November 12, 1980, Waste No. F016 was deleted for 261.31, since EPA is now convinced that the blast furnace and coke oven scrubber sludges pose no significant hazards (page 74888). K063 (sludge from lime treatment of pickle liquor) was also removed from the hazardous list, but is still covered by another section until proved safe.

"The only furnace-related by-product of the steel industry listed as hazardous is the electric-furnace emission control dust or sludge, based on possible high concentrations of hexavalent chromium, lead and cadmium. Individual sources can be tested for toxicity from these materials and cleared from the hazardous classification on an individual plant basis. No steelmaking slags are current classification criteria, or are intended to be included in such classification. All types of slags from the steel industry are being used and have been used for many years."

EPA's own contract research studies performed nearly a decade ago listed slag as non-hazardous under the existing test methods and standards. NSA has not been notified of any change in this posture. If anyone has any information or documentation to the contrary, please forward it, forthwith, to the NSA office.

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Refer to: Federal Register, Vol. 45, No. 98, May 19, 1980, pages 33108-10 and 33123-4. For further information, contact:

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**NATIONAL SLAG  
ASSOCIATION**

## **Iron and Steel Making Slag – Environmentally Responsible Construction Aggregates**

The National Slag Association proves that Iron and Steel Making Slag materials present no threat to human health or to the environment.

### **Challenge:**

The National Slag Association wanted to prove that Iron and Steel making slags are suitable aggregate materials for use in a variety of residential, agricultural, industrial and construction applications.

The slag materials represented by the National Slag Association are generated in the Iron and Steel making process. Blast Furnace (BF) Slag is generated simultaneously with the production of iron on a blast furnace and Steel making Slag is a co-product of the steel produced either in a Basic Oxygen Furnace (BOF) or Electric Arc Furnace (EAF). The slag is removed from the furnace at 1,600°C (3,000°F) and cooled to ambient temperatures prior to being crushed and screened into various sizes of construction aggregates.

Through work with governmental agencies, environmental scientists and toxicologists, Iron and Steel making slag has been approved for use by many environmental regulatory agencies and State Departments of Transportation.

### **Solution:**

Iron and steel slags have been extensively tested using certified laboratories, following USEPA and American Society for Testing Materials (ASTM) procedures. Tests conducted include: the Toxic Characteristic Leaching Procedure (TCLP) EPA Method 1311 test, ASTM Distilled Water Leachate ASTM Method D3987-85, Major Element Bulk Chemistry, Minor Element Bulk Chemistry and other tests. Since iron and steel slag is generated in a 1600° C (3000° F) furnace, organic, semi-volatile, or volatile compounds are not present in iron and steel slag. Chemically iron and steel slag consists primarily of oxides of calcium, iron, silicon, aluminum, magnesium and manganese in complexes of calcium silicates, aluminosilicates and aluminoferrite (primarily with BOF and EAF slag). These compounds are generally similar to those found in the natural  
(over)

environment. The metals in slags are fused together and tightly bound, therefore are not readily liberated from the slag particle or easily leached into the environment.

A Steel Slag Coalition was formed consisting of a group of 63 steel makers and slag processing companies which tested iron and steel slag from 73 different generating sources and subsequently prepared a risk assessment.

Environmental scientists and toxicologists completed an industry-wide "Human Health and Ecological Risk Assessment (HERA)". Based on worst case exposure assumptions the HERA demonstrated that iron and steel slag poses no meaningful threat to human health or the environment when used in a variety of residential, agricultural, industrial and construction applications. Consequently, the metals in the slag matrix are not readily available for uptake by humans, other animals or plants, do not bioaccumulate in the food web and are not expected to bioconcentrate in plant tissue.

Slag has been safely and successfully used as a construction aggregate in many applications such as asphaltic concrete, Portland cement concrete, roadway embankment and shoulders and on unpaved roads, parking lots, walkways, and driveways. Non-construction related applications include the Portland cement production, agricultural applications such as soil remineralization, pH supplement / liming agent, for treating acidic run-off from abandoned mines and for remediation of industrial waste water run-off. Contact your local **National Slag Association member** or the **National Slag Association** for appropriate uses of Iron and Steel Slag.

Iron and steel slag may be applied safely in aquatic environments, such as rivers, lakes or streams without impacting water quality or aquatic life. Prior to using slag in small aquatic bodies or stagnant water, contact the **National Slag Association** for a full **Risk Assessment Analysis** report. A full report is available for a nominal cost.

The U.S. Department of Interior, U.S. Geological Survey tracks mineral industry sales and they report that roughly 19,000,000 tons of iron and steel slag are sold annually for use in construction with a commercial value of \$150 million USD. Slag products are used extensively in the US with more than 50% of the iron and steel slag sold in the United States used for road construction.

Using iron and steel furnace slag will help preserve our natural resources. Based on the numerous environmental tests, studies and reviews by governmental agencies and the iron and steel industry we know iron and steel slag is a safe and valuable resource, and we encourage its use as an environmentally friendly product.

***Developed by the National Slag Association - Environmental Committee***